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#### Cyclobutane derivatives

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The present invention relates to cyclobutane derivatives which contain both a CF<sub>2</sub>O bridge as constituent of their mesogenic skeleton and a butane-1,4-diyl group as part of a spiroalkane unit, to the use thereof as component(s) of liquid-crystalline media, and to liquid-crystal and electro-optical display elements which contain these liquid-crystalline media according to the invention.

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The cyclobutane derivatives according to the invention can be used as components of liquid-crystalline media, in particular for displays based on the principle of the twisted cell, the guest-host effect, the effect of deformation of aligned phases DAP or ECB (electrically controlled birefringence), the IPS effect (in-plane switching) or the effect of dynamic scattering.

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All the substances employed hitherto for this purpose have certain disadvantages, for example inadequate stability to the effect of heat, light or electric fields, or unfavourable elastic and/or dielectric properties.

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The invention thus had the object of finding novel stable liquid-crystalline or mesogenic compounds which are suitable as components of liquid-crystalline media, in particular for TN, STN, IPS and TFT displays.

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A further object of the present invention was to provide liquid-crystalline compounds which have low rotational viscosity, result in an improvement in low-temperature stability in liquid-crystal mixtures, and can be synthesised simply. In particular through the reduction in the rotational viscosity, it should be possible to achieve significantly shorter response times.

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Surprisingly, it has been found that the cyclobutane derivatives according to the invention are eminently suitable as components of liquid-crystalline media. They can be used to obtain stable liquid-crystalline media, particularly suitable for TFT or STN displays.

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The physical properties of the cyclobutane derivatives according to the invention can be varied in broad ranges through a suitable choice of the ring members and/or the terminal substituents. Thus, for example, it is possible to obtain cyclobutane derivatives according to the invention having very low optical anisotropy values or low positive to highly positive dielectric anisotropy values.

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In particular, the cyclobutane derivatives according to the invention are distinguished by high clearing points at the same time as unexpectedly low rotational viscosity.

Liquid-crystalline media having very low optical anisotropy values are of particular importance for reflective and transflective applications, i.e. applications in which the respective LCD experiences no or only supporting backlighting.

The provision of the cyclobutane derivatives according to the invention very generally considerably broadens the range of liquid-crystalline substances which are suitable, from various applicational points of view, for the preparation of liquid-crystalline mixtures.

The cyclobutane derivatives according to the invention have a broad range of applications. Depending on the choice of the substituents, these compounds can serve as base materials of which liquid-crystalline media are predominantly composed; however, it is also possible to add liquid-crystalline base materials from other classes of compound to the cyclobutane derivatives according to the invention in order, for example, to influence the dielectric and/or optical anisotropy of a dielectric of this type and/or to optimise its threshold voltage and/or its viscosity.

In the pure state, the cyclobutane derivatives according to the invention are colourless and form liquid-crystalline mesophases in a temperature range which is favourably located for electro-optical use. They are stable chemically, thermally and to light.

The present invention thus relates to cyclobutane derivatives of the formula I

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$$R^{1}-(A-Z)_{m}$$
  $CF_{2}O$   $(A-Z)_{n}-R^{2}$ 

in which

10  $R^1, R^2$ 

are identical or different and each, independently of one another, denote H, halogen (F, Cl, Br or I) or a linear or branched, optionally chiral alkyl or alkoxy radical having 1 to 15 C atoms which is unsubstituted or mono- or polysubstituted by halogen and in which one or more CH<sub>2</sub> groups may each be replaced, independently of one another, by -O-, -S-, -CO-, -CO-O-, -O-CO-, -CH=CH-, -CH=CF-, -CF=CF-, -C=C- or in such a way that heteroatoms are not linked directly to one another, -CN, -SCN, -NCS, -SF<sub>5</sub>, -SCF<sub>3</sub>, -CF<sub>3</sub>, -CF=CF<sub>2</sub>, -CF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>, -OCF<sub>3</sub>, -OCHF<sub>2</sub>,

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-CF<sub>2</sub>CH<sub>2</sub>CF<sub>3</sub> or -OCH<sub>2</sub>CF<sub>2</sub>CHFCF<sub>3</sub>, is identical or different and in each case, independently of

Α

is identical or different and in each case, independently of one another, denotes

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 a) trans-1,4-cyclohexylene, in which, in addition, one or more non-adjacent CH<sub>2</sub> groups may be replaced by -Oand/or -S- and in which, in addition, one or more H atoms may be replaced by F,

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b) 1,4-phenylene, in which one or two CH groups may be replaced by N and in which, in addition, one or more H atoms may be replaced by halogen (F, Cl, Br or I), -CN, -CH<sub>3</sub>, -CHF<sub>2</sub>, -CH<sub>2</sub>F, -OCH<sub>3</sub>, -OCHF<sub>2</sub> or -OCF<sub>3</sub>,

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c) a radical from the group bicyclo[1.1.1]pentane-1,3-diyl, bicyclo[2.2.2]octane-1,4-diyl, spiro[3.3]heptane-2,6-diyl,

naphthalene-2,6-diyl, decahydronaphthalene-2,6-diyl, 1,2,3,4-tetrahydronaphthalene-2,6-diyl and piperidine-1,4-diyl, or

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- d) 1,4-cyclohexenylene,
- is identical or different and in each case, independently of one another, denotes -O-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -CO-O-, -O-CO-, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF-, -CF=CF-COO-, -O-CO-CF=CF-, -C=C- or a single bond,
  - m, n are identical or different and, independently of one another, denote 0, 1 or 2, preferably m = 0 or 1 and n = 1 or 2, and
  - o denotes 0 or 1.

The present invention furthermore relates to the use of compounds of the formula I as component(s) of liquid-crystalline media.

The present invention likewise relates to liquid-crystalline media having at least two liquid-crystalline components which comprise at least one compound of the formula I.

- The present invention also relates to liquid-crystal display elements, in particular electro-optical display elements, which contain, as dielectric, a liquid-crystalline medium according to the invention.
- Particular preference is given to reflective and transflective liquid-crystal display elements and other liquid-crystal displays of low birefringence Δn, so-called "low Δn mode displays", such as, for example, reflective and transflective TN displays.
- The meaning of the formula I includes all isotopes of the chemical elements bound in the compounds of the formula I. In enantiomerically pure

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or enriched form, the compounds of the formula I are also suitable as chiral dopants and in general for achieving chiral mesophases.

Above and below, R<sup>1</sup>, R<sup>2</sup>, A, Z, m, n and o have the meaning indicated, unless expressly stated otherwise. If the radicals A and Z occur more than once, they may, independently of one another, adopt identical or different meanings.

Preference is given to compounds of the formula I in which R<sup>1</sup> is H or a linear alkyl radical having 1 to 10 C atoms.

Preference is likewise given to compounds of the formula I in which R<sup>2</sup> denotes H, a linear alkoxy radical having 1 to 10 C atoms, -F, -CI, -CF<sub>3</sub>, -OCF<sub>3</sub>, -OCHF<sub>2</sub>, -CN, -NCS or -SF<sub>5</sub>, particularly preferably -OC<sub>2</sub>H<sub>5</sub>, -F, -CF<sub>3</sub>, -OCF<sub>3</sub> or -CN.

Preferred compounds of the formula I are compounds of the sub-formula Ia

$$R^{1}$$
-(A-Z)<sub>m</sub>  $CF_{2}O$  -(A-Z)<sub>n</sub>- $R^{2}$  la

and compounds of the sub-formula lb

$$R^{1}-(A-Z)_{m} - CF_{2}O - (A-Z)_{n}-R^{2} \qquad Ib$$

in which  $R^1$ ,  $R^2$ , A, Z, m and n have the meanings indicated above.

Z preferably denotes - $CH_2CH_2$ -, -CH=CH-, - $C\equiv C$ -, - $CF_2CF_2$ -, -CF=CF-, - $CF_2O$ - or a single bond, particularly preferably a single bond.

For reasons of simplicity, Cyc below denotes a 1,4-cyclohexylene radical,
Che denotes a 1,4-cyclohexenylene radical, Dio denotes a 1,3-dioxane2,5-diyl radical, Dit denotes a 1,3-dithiane-2,5-diyl radical, Phe denotes a

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1,4-phenylene radical, Pyd denotes a pyridine-2,5-diyl radical, Pyr denotes a pyrimidine-2,5-diyl radical, Bco denotes a bicyclo[2.2.2]octylene radical and Dec denotes a decahydronaphthalene-2,6-diyl radical, where Cyc and/or Phe may be unsubstituted or mono- or polysubstituted by CH<sub>3</sub>, Cl, F or CN.

A preferably denotes Phe, Cyc, Che, Pyd, Pyr or Dio, and particularly preferably Phe or Cyc.

10 Phe preferably denotes

The terms 1,3-dioxane-2,5-diyl and Dio each encompass the two positional isomers

$$-$$
 and  $0$ 

The cyclohexene-1,4-diyl group preferably has the following structures:

Particularly preferred compounds of the formula la include the following formulae:

$$R^{1}$$
 $CF_{2}O$ 
 $L^{4}$ 
 $L^{1}$ 
 $R^{2}$ 
laa

$$R^{1} \longrightarrow Z \longrightarrow CF_{2}O \longrightarrow L^{2} \longrightarrow R^{2}$$
 lab

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$$R^1$$
  $CF_2O$   $CF_$ 

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad lad$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{2} \longrightarrow R^{2}$$
 lae

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2}$$
Iaf

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$$R^{1} \longrightarrow A \longrightarrow CF_{2}O \longrightarrow L^{2} \longrightarrow R^{2}$$
 lag

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$$R^1$$
  $CF_2O$   $CF_2O$   $R^2$  lai

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$
 lak

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad lal$$

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$$R^{1} - CF_{2}O - CF_{2}O - R^{2} - Iam$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad lan$$

$$R^{1} \longrightarrow A \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$
 lao

$$20 \qquad R^{1} \qquad CF_{2}O \qquad CF_{2}O \qquad Iap$$

Particularly preferred compounds of the formula lb include the following formulae:

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2}$$
 Iba

$$R^{1} \longrightarrow Z \longrightarrow CF_{2}O \longrightarrow R^{2} \longrightarrow R^{2}$$
 lbb

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad Ibc$$

$$10 \qquad R^{1} \longrightarrow CF_{2}O \longrightarrow L^{2} \qquad Ibd$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad \text{lbe}$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2}$$

$$L^{4} \longrightarrow L^{1}$$

$$R^{2} \longrightarrow R^{2}$$

$$L^{3} \longrightarrow L^{2}$$

$$R^{4} \longrightarrow L^{1}$$

$$R^{1} \longrightarrow A \longrightarrow CF_{2}O \longrightarrow L^{1} \longrightarrow R^{2}$$
 lbg

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$

$$L^{5}L^{3} \longrightarrow L^{2}$$
Ibi

$$R^{1} \longrightarrow Z \longrightarrow CF_{2}O \longrightarrow L^{5}L^{3} \longrightarrow L^{2}$$
 Ibj

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$

$$L^{5}L^{3} \longrightarrow L^{2}$$

$$L^{5}L^{3} \longrightarrow L^{2}$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \longrightarrow R^{2} \qquad Ibl$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$
 Ibm

$$R^{1} \longrightarrow CF_{2}O \longrightarrow L^{6}L^{4} \longrightarrow L^{1}$$

$$L^{5}L^{3} \longrightarrow L^{2}$$
Ibn

$$R^1$$
  $CF_2O$   $CF_2O$ 

$$R^1$$
  $CF_2O$   $CF_2O$ 

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in which  $R^1$ ,  $R^2$ , A and Z have the meanings indicated above, and  $L^1$ ,  $L^2$ ,  $L^3$ ,  $L^4$ ,  $L^5$  and  $L^6$ , are identical or different and, independently of one another, denote H or F.

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Preference is given to compounds of the formulae laa to lap and lba to lbp in which R<sup>1</sup> denotes H or a linear alkyl or alkoxy radical having 1 to 10 C atoms or alkenyl or alkenyloxy having 2 to 10 C atoms.

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Preference is likewise given to compounds of the formulae laa to lap and lba to lbp in which  $R^2$  denotes -F, -CF<sub>3</sub>, -OCF<sub>3</sub>, -CN, -NCS, -SF<sub>5</sub> or -OC<sub>2</sub>H<sub>5</sub>.

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Particular preference is given to compounds of the formulae laa to lah and lba to lbh in which  $R^2$  denotes -F, -CF<sub>3</sub>, -OCF<sub>3</sub>, -CN, -NCS or -SF<sub>5</sub>,  $L^1$  and  $L^2$ , are identical or different and, independently of one another, denote F or H, and  $L^3$  and  $L^4$  denote H.

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Particular preference is given to compounds of the formulae laa to lah and lba to lbh in which  $R^2$  is  $-OC_2H_5$ ,  $L^2$  and  $L^3$ , are identical or different and are , independently of one another, F or H, and  $L^1$  and  $L^4$  are H.

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Particular preference is given to compounds of the formulae lai to lap and lbi to lbp in which  $R^2$  denotes -F, -CF<sub>3</sub>, -OCF<sub>3</sub>, -CN, -NCS or -SF<sub>5</sub>,  $L^1$ ,  $L^2$ ,  $L^5$  and  $L^6$ , are identical or different and, independently of one another, denote F or H, and  $L^3$  and  $L^4$  denote H.

Particular preference is given to compounds of the formulae lai to lap and lbi to lbp in which  $R^2$  denotes  $-OC_2H_5$ ,  $L^2$ ,  $L^3$  and  $L^6$ , are identical or different and, independently of one another, denote F or H, and  $L^1$ ,  $L^4$  and  $L^5$  denote H.

In the compounds of the formulae lab, laj, lbb and lbj, Z preferably denotes -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>O- or a single bond, particularly preferably a single bond.

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In the compounds of the formulae lag, lao, lbg and lbo, A is preferably

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$$\longrightarrow$$
 or  $\longrightarrow$   $\longrightarrow$ 

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If R<sup>1</sup> and/or R<sup>2</sup> in the formulae above and below denote an alkyl radical, this may be straight-chain or branched. It is particularly preferably straight-chain, has 2, 3, 4, 5, 6 or 7 C atoms and accordingly denotes ethyl, propyl, butyl, pentyl, hexyl or heptyl, furthermore methyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl or pentadecyl.

If R<sup>1</sup> and/or R<sup>2</sup> denotes an alkyl radical in which one CH<sub>2</sub> group has been replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain and has 1 to 10 C atoms. The first CH<sub>2</sub> group of this alkyl radical has particularly preferably been replaced by -O-, so that the radical R<sup>1</sup> and/or R<sup>2</sup> attains the meaning alkoxy and, in particular, denotes methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy or nonyloxy.

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Furthermore, a  $CH_2$  group elsewhere may also be replaced by -O-, so that the radical  $R^1$  and/or  $R^2$  preferably denotes straight-chain 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl),

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2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

- If R<sup>1</sup> and/or R<sup>2</sup> denotes an alkyl radical in which one CH<sub>2</sub> group has been replaced by -CH=CH-, this may be straight-chain or branched. It is preferably straight-chain and has 2 to 10 C atoms. Accordingly, it denotes vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl, or dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or -9-enyl.
- Preferred alkenyl groups are  $C_2$ - $C_7$ -1E-alkenyl,  $C_4$ - $C_7$ -3E-alkenyl,  $C_5$ - $C_7$ -4-alkenyl,  $C_6$ - $C_7$ -5-alkenyl and  $C_7$ -6-alkenyl, particularly preferably  $C_2$ - $C_7$ -15 1E-alkenyl,  $C_4$ - $C_7$ -3E-alkenyl and  $C_5$ - $C_7$ -4-alkenyl.

Examples of particularly preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4

If R<sup>1</sup> and/or R<sup>2</sup> denotes an alkyl radical in which one CH<sub>2</sub> group has been replaced by -O- and one has been replaced by -CO-, these are preferably adjacent. These thus contain an acyloxy group -CO-O- or an oxycarbonyl group -O-CO-. These are particularly preferably straight-chain and have 2 to 6 C atoms.

Accordingly, they denote in particular acetoxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetoxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetoxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetoxypropyl, 3-propionyloxypropyl, 4-acetoxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl, propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxy-

carbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)propyl, 3-(ethoxycarbonyl)propyl or 4-(methoxycarbonyl)butyl.

If R<sup>1</sup> and/or R<sup>2</sup> denotes an alkyl radical in which one CH<sub>2</sub> group has been replaced by unsubstituted or substituted -CH=CH- and an adjacent CH<sub>2</sub> group has been replaced by CO, CO-O or O-CO, this may be straight-chain or branched. It is preferably straight-chain and has 4 to 13 C atoms. Accordingly, it particularly preferably denotes acryloyloxymethyl, 2-acryloyloxyethyl, 3-acryloyloxypropyl, 4-acryloyloxybutyl, 5-acryloyloxypentyl, 6-acryloyloxyhexyl, 7-acryloyloxyheptyl, 8-acryloyloxyoctyl, 9-acryloyloxynonyl, 10-acryloyloxydecyl, methacryloyloxymethyl, 2-methacryloyloxyethyl, 3-methacryloyloxypropyl, 4-methacryloyloxybutyl, 5-methacryloyloxypentyl, 6-methacryloyloxyhexyl, 7-methacryloyloxyheptyl, 8-methacryloyloxyoctyl or 9-methacryloyloxynonyl.

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If  $R^1$  and/or  $R^2$  denotes an alkyl or alkenyl radical which is monosubstituted by CN or CF<sub>3</sub>, this radical is preferably straight-chain and substitution by CN or CF<sub>3</sub> is in the  $\omega$ -position.

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If  $R^1$  and/or  $R^2$  denotes an alkyl radical which is at least monosubstituted by halogen, this radical is preferably straight-chain. Halogen is preferably F or Cl. In the case of polysubstitution, halogen is preferably F. The resultant radicals also include perfluorinated radicals. In the case of monosubstitution, the fluorine or chlorine substituent can be in any desired position, but is preferably in the  $\omega$ -position.

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Compounds of the formula I having a branched wing group R<sup>1</sup> and/or R<sup>2</sup> may occasionally be of importance owing to better solubility in the conventional liquid-crystalline base materials, but in particular as chiral dopants if they are optically active. Smectic compounds of this type are suitable as components of ferroelectric materials.

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Branched groups of this type generally contain not more than one chain branch. Preferred branched radicals R<sup>1</sup> and/or R<sup>2</sup> are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propyl-

pentyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylbutoxy, 2-methylpentyloxy, 3-methylpentyloxy, 2-ethylhexyloxy, 1-methylhexyloxy and 1-methylheptyloxy.

The formula I encompasses both the racemates of these compounds and the optical antipodes, and mixtures thereof.

Of the compounds of the formula I and the sub-formulae, preference is given to those in which at least one of the radicals present therein has one of the preferred meanings indicated.

The compounds of the formula I are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can be made here of variants which are known per se, but are not mentioned here in greater detail.

The compounds of the formula I can be prepared, for example, in accordance with the following reaction schemes or analogously thereto. Further synthetic methods are given in the examples.

In schemes 1 to 4, R<sup>1</sup>, R<sup>2</sup>, A, Z, n, m and o have the meanings indicated above. L<sup>1</sup>, L<sup>2</sup>, L<sup>3</sup>, L<sup>4</sup>, L<sup>5</sup> and L<sup>6</sup>, are identical or different and, independently of one another, denote H or F.

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Scheme 1: (o = 0 or 1)

Synthesis disclosed in WO 02/48073 A1.

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$$R^{1}-(A-Z)_{m}$$
 $R^{1}-(A-Z)_{m}$ 
 $R^{1}-(A-Z)_{m}$ 

Scheme 2: (o = 0 or 1)

Synthesis disclosed in WO 01/64667 A1, in P. Kirsch, M. Bremer,
A. Taugerbeck, T. Wallmichrath, Angew. Chem. Int. Ed. Engl. 2001, 40,
1480-1484, and in the literature cited in this article.

$$R^{1}-(A-Z)_{m} \xrightarrow{\text{Po}} COOH$$

$$R^{1}-(A-Z)_{m} \xrightarrow{\text{Po}} S^{+} TfO^{-}$$

$$R^{1}-(A-Z)_{m} \xrightarrow{\text{Po}} COOH$$

$$R^{1}-(A-Z)_{m} \xrightarrow{\text{Po}} COOH$$

Scheme 3: (o = 0 or 1)

Synthesis disclosed in EP 1 182 186 A2.

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$$R^{1}-(A-Z)_{m}$$
  $O-(A-Z)_{n}-R^{2}$ 

15 Scheme 4: (o = 0 or 1)
Synthesis disclosed in EP 1 182 186 A2.

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 $R^{1}-(A-Z)_{m} - (A-Z)_{n} - (A-Z)_{n} - R$ 



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$$R^{1}-(A-Z)_{m}$$
  $O-(A-Z)_{n}-R^{2}$ 

The starting materials are either known or can be prepared analogously to known compounds.

If desired, the starting materials can also be formed in situ by not isolating them from the reaction mixture, but instead immediately converting them further into the compounds of the formula I.

5 The liquid-crystalline media according to the invention preferably comprise 2 to 40, particularly preferably 4 to 30, components as further constituents besides one or more compounds according to the invention. In particular, these media comprise 7 to 25 components besides one or more compounds according to the invention. These further constituents are preferably 10 selected from nematic or nematogenic (monotropic or isotropic) substances, in particular substances from the classes of the azoxybenzenes, benzylideneanilines, biphenyls, terphenyls, phenyl or cyclohexyl benzoates, phenyl or cyclohexyl esters of cyclohexanecarboxylic acid, phenyl or cyclohexyl esters of cyclohexylbenzoic acid, phenyl or cyclohexyl esters of cyclo-15 hexylcyclohexanecarboxylic acid, cyclohexylphenyl esters of benzoic acid, of cyclohexanecarboxylic acid or of cyclohexylcyclohexanecarboxylic acid, phenylcyclohexanes, cyclohexylbiphenyls, phenylcyclohexylcyclohexanes, cyclohexylcyclohexanes, cyclohexylcyclohexylcyclohexenes, 1,4-biscyclohexylbenzenes, 4,4'-biscyclohexylbiphenyls, phenyl- or cyclohexylpyrimi-20 dines, phenyl- or cyclohexylpyridines, phenyl- or cyclohexyldioxanes, phenylor cyclohexyl-1,3-dithianes, 1,2-diphenylethanes, 1,2-dicyclohexylethanes, 1-phenyl-2-cyclohexylethanes, 1-cyclohexyl-2-(4-phenylcyclohexyl)ethanes, 1-cyclohexyl-2-biphenylylethanes, 1-phenyl-2-cyclohexylphenylethanes, optionally halogenated stilbenes, benzyl phenyl ethers, tolans and 25 substituted cinnamic acids. The 1,4-phenylene groups in these compounds may also be fluorinated.

The most important compounds suitable as further constituents of the media according to the invention can be characterised by the formulae 1, 2, 3, 4 and 5:

	R'-L-E-R"	1
	R'-L-COO-E-R"	2
	R'-L-OOC-E-R"	3
35	R'-L-CH <sub>2</sub> CH <sub>2</sub> -E-R"	4
	R'-L-C≡C-E-R"	5

In the formulae 1, 2, 3, 4 and 5, L and E, which may be identical or different, each, independently of one another, denote a divalent radical from the group formed by -Phe-, -Cyc-, -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -Pyr-, -Dio-, -G-Phe- and -G-Cyc- and their mirror images, where Phe denotes unsubstituted or fluorine-substituted 1,4-phenylene, Cyc denotes trans-1,4-cyclohexylene or 1,4-cyclohexenylene, Pyr denotes pyrimidine-2,5-diyl or pyridine-2,5-diyl, Dio denotes 1,3-dioxane-2,5-diyl and G denotes 2-(trans-1,4-cyclohexyl)ethyl.

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One of the radicals L and E preferably denotes Cyc, Phe or Pyr. E preferably denotes Cyc, Phe or Phe-Cyc. The media according to the invention preferably comprise one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which L and E are selected from the group Cyc, Phe and Pyr and simultaneously one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which one of the radicals L and E is selected from the group Cyc, Phe and Pyr and the other radical is selected from the group -Phe-Phe-, -Phe-Cyc-, -Cyc-Cyc-, -G-Phe-and -G-Cyc-, and optionally one or more components selected from the compounds of the formulae 1, 2, 3, 4 and 5 in which the radicals L and E are selected from the group -Phe-Cyc-, -Cyc-Cyc-, -G-Phe- and -G-Cyc-.

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R' and/or R" each, independently of one another, denote alkyl, alkenyl, alkoxy, alkoxyalkyl, alkenyloxy or alkanoyloxy having up to 8 C atoms, -F, -Cl, -CN, -NCS, -(O)<sub>i</sub>CH<sub>3-(k+l)</sub>F<sub>k</sub>Cl<sub>l</sub>, where i denotes 0 or 1, k and l, are identical or different and, independently of one another, denote 0, 1, 2 or 3, and the following applies to the sum (k + l):  $1 \le (k + l) \le 3$ .

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In a smaller sub-group of the compounds of the formulae 1, 2, 3, 4 and 5, R' and R" each, independently of one another, denote alkyl, alkenyl, alkoxy, alkoxyalkyl, alkenyloxy or alkanoyloxy having up to 8 C atoms. This smaller sub-group is called group A below, and the compounds are referred to by the sub-formulae 1a, 2a, 3a, 4a and 5a. In most of these compounds, R' and R" are different from one another, one of these radicals usually being alkyl, alkenyl, alkoxy or alkoxyalkyl.

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In another smaller sub-group of the compounds of the formulae 1, 2, 3, 4 and 5, which is known as group B, R" is -F, -Cl, -NCS or -(O)<sub>i</sub>CH<sub>3-(k+l)</sub>F<sub>k</sub>Cl<sub>l</sub>, where i denotes 0 or 1, k and l, are identical or different and, independently of one another, denote 1, 2 or 3, and the following applies to the sum (k + l):  $1 \le (k + l) \le 3$ . The compounds in which R" has this meaning are referred to by the sub-formulae 1b, 2b, 3b, 4b and 5b. Particular preference is given to those compounds of the sub-formulae 1b, 2b, 3b, 4b and 5b in which R" denotes -F, -Cl, -NCS, -CF<sub>3</sub>, -OCHF<sub>2</sub> or -OCF<sub>3</sub>.

In the compounds of the sub-formulae 1b, 2b, 3b, 4b and 5b, R' has the meaning indicated for the compounds of the sub-formulae 1a to 5a and is preferably alkyl, alkenyl, alkoxy or alkoxyalkyl.

In a further smaller sub-group of the compounds of the formulae 1, 2, 3, 4 and 5, R" denotes -CN. This sub-group is referred to below as group C, and the compounds of this sub-group are correspondingly described by sub-formulae 1c, 2c, 3c, 4c and 5c. In the compounds of the sub-formulae 1c, 2c, 3c, 4c and 5c, R' has the meaning indicated for the compounds of the sub-formulae 1a to 5a and preferably denotes alkyl, alkoxy or alkenyl.

Besides the preferred compounds of groups A, B and C, other compounds of the formulae 1, 2, 3, 4 and 5 having other variants of the proposed substituents are also customary. All these substances are obtainable by methods which are known from the literature or analogously thereto.

Besides the compounds of the formula I according to the invention, the media according to the invention preferably comprise one or more compounds selected from groups A, B and/or C. The proportions by weight of the compounds from these groups in the media according to the invention are preferably

group A: 0 to 90%, preferably 20 to 90%, in particular 30 to 90%

group B: 0 to 80%, preferably 10 to 80%, in particular 10 to 65%

group C: 0 to 80%, preferably 5 to 80%, in particular 5 to 50%,

where the sum of the proportions by weight of the group A, B and/or C compounds present in the respective media according to the invention is preferably 5 to 90% and in particular 10 to 90%.

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The media according to the invention preferably comprise 1 to 40%, particularly preferably 5 to 30%, of the compounds of the formula I according to the invention. Preference is furthermore given to media comprising more than 40%, particularly preferably 45 to 90%, of compounds of the formula I according to the invention. The media preferably comprise three, four or five compounds according to the invention.

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The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner which is conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, preferably at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing. It is furthermore possible to prepare the mixtures in other conventional manners, for example by using premixes, for example homologue mixtures, or using so-called "multibottle" systems.

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The dielectrics may also comprise further additives known to the person skilled in the art and described in the literature. For example, 0 to 15%, preferably 0 to 10%, of pleochroic dyes and/or chiral dopants can be added. The individual compounds added are employed in concentrations of 0.01 to 6%, preferably 0.1 to 3%. However, the concentration data of the other constituents of the liquid-crystal mixtures, i.e. the liquid-crystalline or mesogenic compounds are indicated without taking into account the concentration of these additives.

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In the present application and in the following examples, the structures of the liquid-crystal compounds are indicated by means of acronyms, the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals  $C_nH_{2n+1}$  and  $C_mH_{2m+1}$  are straight-chain

alkyl radicals having n and m C atoms respectively. n and m are an integers, preferably 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12, where n = m or n  $\neq$  m. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is indicated. In individual cases, the acronym for the parent structure is followed, separated by a dash, by a code for the substituents  $R^{1*}$ ,  $R^{2*}$ ,  $L^{1*}$  and  $L^{2*}$ :

40	Code for R <sup>1*</sup> , R <sup>2*</sup> , L <sup>1*</sup> , L <sup>2*</sup>	R <sup>1*</sup>	R <sup>2*</sup>	L <sup>1*</sup>	L <sup>2*</sup>
10	nm	C <sub>n</sub> H <sub>2n+1</sub>	C <sub>m</sub> H <sub>2m+1</sub>	Н	Н
	nOm	$C_nH_{2n+1}$	$OC_mH_{2m+1}$	Н	Н
	nO.m	$OC_nH_{2n+1}$	$C_mH_{2m+1}$	Н	Н
	nN	$C_nH_{2n+1}$	CN	Н	Н
15	nN.F	$C_nH_{2n+1}$	CN .	н	F
	nN.F.F	$C_nH_{2n+1}$	CN	F	F
	nF	$C_nH_{2n+1}$	F	Н	Н
	nOF	$OC_nH_{2n+1}$	F	Н	Н
20	nF.F	$C_nH_{2n+1}$	F	Н	F
	nmF	$C_nH_{2n+1}$	$C_mH_{2m+1}$	Н	F
	nCF <sub>3</sub>	$C_nH_{2n+1}$	CF <sub>3</sub>	Н	Н
	nOCF <sub>3</sub>	$C_nH_{2n+1}$	OCF <sub>3</sub>	Н	Н
0.5	n-Vm	$C_nH_{2n+1}$	-CH=CH-C <sub>m</sub> H <sub>2m+1</sub>	Н	Н
25	nV-Vm	C <sub>n</sub> H <sub>2n+1</sub> -CH=CH-	-CH=CH-C <sub>m</sub> H <sub>2m+1</sub>	Н	Н

Preferred mixture components are indicated in Tables A and B.

#### Table A:

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$$R^{1^*} - O_N^{N} - O_{L^{2^*}}^{L^{1^*}} \qquad \qquad R^{1^*} - O_N^{N} - O_{L^{2^*}}^{L^{1^*}}$$

$$PYP \qquad \qquad PYRP$$

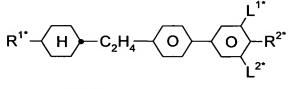
$$\mathsf{R}^{1^{\star}} \hspace{-2pt} - \hspace{-2pt} \mathsf{C}_2 \mathsf{H}_{\hspace{-2pt} 4} \hspace{-2pt} - \hspace{-2pt} \mathsf{C}_2^{1^{\star}}$$

$$R^{1^*}$$
  $H$   $O$   $R^{2^*}$   $L^{2^*}$ 

5 **EPCH** 

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$$R^{1^*}$$
  $O$   $C \equiv C$   $O$   $C$   $R^{2^*}$ 



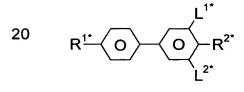
PTP

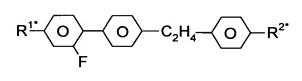
**BECH** 

$$R^{1^*} - H - O - C_2H_4 - O - R^{2^*} R^{1^*} - H - O - H - R^{2^*}$$

**EBCH** 

CPC





В

FET-nF

$$R^{1*} H O R^{2}$$

CGG

CGU

$$R^{1^{*}} \underbrace{H} \underbrace{O}_{F} R^{2^{*}}$$

CFU

## Table B:

$$C_{n}H_{2n+1} - H - O - C_{m}H_{2m+1} C_{n}H_{\overline{2n+1}} + O - F$$

## BCH-n.Fm

## CFU-n-F

$$C_nH_{2n+1}$$
  $H$   $C_2H_4$   $O$   $C_mH_{2m+1}$ 

I-nm

$$C_nH_{2n+1}$$
  $H$   $O$   $F$   $C_nH_{2n+1}$   $H$   $O$   $F$ 

## BCH-nF.F

BCH-nF.F.F

$$C_nH_{2n+1}$$
  $H$   $O$   $O$   $H$   $C_mH_{2m+1}$ 

CBC-nmF

$$C_nH_{2n+1}$$
  $H$   $C_2H_4$   $O$   $C_mH_{2m+1}$ 

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## **ECCP-nm**

$$C_nH_{2n+1}$$
  $H$   $CH_2O-C_mH_{2m+1}$ 

30 CCH-n1Em

$$C_nH_{2n+1}$$
  $H$   $COO$   $H$   $C_mH_{2m+1}$ 

OS-nm

$$C_nH_{2n+1}$$
  $H$   $COO$   $F$   $F$ 

5 CCZU-n-F

$$C_nH_{\overline{2n+1}}H$$
  $H$   $COO$   $H$   $C_mH_{2m+1}$ 

 $C_nH_{\overline{2n+1}}$  H

CC-n-V

CH-nm

$$C_nH_{2n+1}H$$
  $O$   $F$   $F$   $F$ 

 $C_nH_{2n+1}H$  O O F

15 CGU-n-F

$$C_nH_{2n+1}H$$
  $O$   $F$   $F$ 

CDU-n-F

20 CGG-n-F

$$C_nH_{2n+1}$$
  $H$   $O$   $OCF_3$ 

CDU-n-OD

$$C_nH_{2n+1}H$$
  $H$   $O$   $OCHF_2$ 

25 CCP-nOCF<sub>3</sub>

$$C_nH_{2n+1}H$$
  $H$   $O$   $F$ 

CCP-nOCF<sub>2</sub>.F

$$C_nH_{2n+1}H$$
  $H$   $O$   $OCF_3$ 

CCP-nF.F.F

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CCP-nOCF<sub>3</sub>.F

$$C_nH_{\overline{2n+1}}H$$
  $CF_2O$   $O$   $F$   $C_nH_{2n+1}$   $H$   $CF_2O$   $H$   $O$   $F$ 

5 CCQU-n-F

$$C_nH_{\overline{2n+1}}$$
  $O$   $F$ 

Dec-U-n-F

$$C_nH_{\overline{2n+1}}O$$
 $F$ 
 $O$ 
 $F$ 
 $F$ 

CQCU-n-F

GPTU-n-F

$$C_nH_{\overline{2n+1}}H$$
 COO  $O$   $F$   $F$   $F$ 

CZGU-n-F

**CC-1V-V1** 

$$C_nH_{\overline{2n+1}}H$$

CC-n-V1

$$C_nH_{\overline{2n+1}}H$$
 $H$ 
 $F$ 

CCTU-n-F

$$C_nH_{2n+1}$$
  $H$   $CH_2CH_2$   $H$   $O$   $OCF_3$   $CECG-n-OT$ 

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$$C_nH_{2n+1}$$
  $H$   $-CH_2CH_2$   $H$   $O$   $-OCF_3$ 

35 CECU-n-OT

$$C_nH_{2n+1} - \underbrace{H} - CF_2O - \underbrace{O} - \underbrace{H} - C_mH_{2m+1}$$

CCQPC-n-m

## Table C:

Table C shows possible dopants which are preferably added to the mixtures according to the invention.

$$C_2H_5$$
- $\overset{*}{C}H$ - $CH_2$ - $O$ - $O$ - $CN$ 
 $CH_3$ 

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**CB 15** 

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**CM 21** 

C 15

**CM 33** 

30 
$$C_6H_{13}$$
 O COO O COO-CH- $C_6H_{15}$ 

**R/S 811** 

5 **CM 44** 

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$$C_5H_{11} \hspace{-0.1cm} \begin{array}{c} O \\ O \\ \end{array} \hspace{-0.1cm} \begin{array}{c} O \\ O \\ C_2H_5 \end{array} \hspace{-0.1cm} \begin{array}{c} C_8H_{17}O \hspace{-0.1cm} \begin{array}{c} O \\ O \\ \end{array} \hspace{-0.1cm} \begin{array}{c} O \\ O \\ C_2H_5 \end{array} \hspace{-0.1cm} \begin{array}{c} O \\ O \\ \end{array} \hspace{-0.1cm} \begin{array}{c} O \\ O \\ C_2H_5 \end{array} \hspace{-0.1cm} \begin{array}{c$$

CM 45 CM 47

H<sub>3</sub>C 
$$CH_3$$
 $C_8H_{17}$ 
 $C_8H_{17}$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

 $C_3H_7 \longrightarrow H \longrightarrow H \longrightarrow O \longrightarrow CH-C_6H_{15}$ 

CN

25 R/S 2011

Particular preference is given to mixtures according to the invention which, besides one or more compounds of the formula I, comprise two, three or more compounds selected from Table B.

The following examples are intended to explain the invention without limiting it. Above and below, percentages are per cent by weight. All temperatures are given in degrees Celsius. m.p. denotes melting point and cl.p. = clearing point. Furthermore, C = crystalline state, N = nematic phase, Sm = smectic phase and I = isotropic phase. The data between these symbols

represent the transition temperatures.  $\Delta n$  denotes optical anisotropy (589 nm, 20°C), and  $\Delta \varepsilon$  the dielectric anisotropy (1 kHz, 20°C).

The  $\Delta n$  and  $\Delta \epsilon$  values of the compounds according to the invention were obtained by extrapolation from liquid-crystalline mixtures which consisted of 10% of the respective compound according to the invention and 90% of the commercially available liquid crystal ZLI 4792 (Merck, Darmstadt).

"Conventional work-up" means that water is added if necessary, the mixture is extracted with methylene chloride, diethyl ether or toluene, the phases are separated, the organic phase is dried and evaporated, and the product is purified by distillation under reduced pressure or crystallisation and/or chromatography.

Above and below, the following abbreviations are used:

DBH 1,3-dibromo-5,5-dimethylhydantoin

DMF dimethylformamide

LDA Lithium diisopropylamide

20 n-BuLi n-butyllithium

RT room temperature (about 20°C)

THF tetrahydrofuran

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#### Example 1

The compound of the following formula

 $C_3H_7 - CF_2O - F - Iab$ 

2-(difluoro[3,4,5-trifluorophenyl]oxymethyl)-6-(4-propylcyclohexyl)spiro-[3.3]heptane [7]

is prepared as follows:

15  $C_{3}H_{7} \longrightarrow A_{1}D \longrightarrow C_{3}H_{7} \longrightarrow A_{2}D \longrightarrow C_{3}H_{7} \longrightarrow A_{3}D \longrightarrow C_{3}H_{7} \longrightarrow A_{4}D \longrightarrow A_{5}D \longrightarrow$ 

Reagents and reaction conditions: a) trichloroacetyl chloride, Zn, ether; b) Zn, HOAc; c)  $(Ph_3P)CH^{\dagger}Br^{\dagger}$ , KOtBu, THF; 2-trimethylsilyl-1,3-dithiane, nBuLi, THF, -78°C  $\rightarrow$  RT; e) 1. 3,4,5-trifluorophenol, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, -78°C; 2. Et<sub>3</sub>N·3HF, DBH, 78°C  $\rightarrow$  RT.

#### Step 1

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2-(6-{4-n-Propylcyclohexyl}spiro[3.3]hept-2-ylidene)[1,3]dithiane 6

15.5 g (80.3 mmol) of 2-trimethylsilyl-1,3-dithiane are dissolved in 150 ml of THF, and 51 ml (80.3 mmol) of n-BuLi (15 per cent in hexane) are rapidly added dropwise at -70°C. The batch is subsequently allowed to thaw to 0°C over the course of 4 hours, stirred for 10 minutes without cooling and re-cooled to -70°C, and a solution of 17.0 g (72.5 mmol) of 6-(4-n-propylcyclohexyl)spiro[3.3]heptan-2-one 5 in 50 ml of THF is added dropwise. The batch is left to stir overnight at room temperature, hydrolysed using saturated sodium hydrogencarbonate solution and extracted with dichloromethane. The combined organic phases are washed with water and dried over sodium sulfate. The solvent is removed under reduced pressure, and the crude product is recrystallised from n-heptane. The dithioacetal 6 is obtained as colourless flakes.

#### Step 2

10.0 g (29.7 mmol) of the dithioacetal 6 are dissolved in 100 ml of dichloro-20 methane, and 2.6 ml (30.0 mmol) of trifluoromethanesulfonic acid are added dropwise with ice/common salt cooling. After 5 minutes, the cooling is removed, and the batch is stirred at room temperature for 45 minutes. The batch is subsequently cooled to -70°C, a mixture of 7.5 ml (54.0 mmol) of triethylamine and 6.67 g (45.0 mmol) of trifluorophenol in 25 30 ml of dichloromethane is added, and the mixture is stirred at -70°C for 1 hour. 24.2 ml (0.150 mol) of triethylamine tris(hydrofluoride) are then added, and, after 5 minutes, 42.9 g (0.150 mol) of DBH, suspended in 60 ml of dichloromethane, are added in portions over the course of about 30 minutes. After 90 minutes, the batch is allowed to thaw and is hydro-30 lysed using 1M sodium hydroxide solution and aqueous hydrogen sulfite solution. The organic phase is separated off, washed with saturated sodium chloride solution and dried over sodium sulfate. The solvent is removed under reduced pressure, and the residue is filtered through silica gel with n-heptane, giving the spiro compound 7 as a colourless solid of 35 melting point: 43°C.

C 43 N 46.6 I

 $\Delta \varepsilon = 9.1$ 

 $\Delta n = 0.0668$ 

 $\gamma_1 = 132 \text{ mPa·s}$ 

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<sup>19</sup>F-NMR (235 MHz, CDCl<sub>3</sub>)

 $\delta$  = -79.2 ppm (d,  ${}^{3}J_{F,H}$  = 10.6 Hz, 2 F, CF<sub>2</sub>O), -133.2 (m<sub>c</sub>, 2 F, Ar-F), -164.7 (tt,  ${}^{3}J_{F,F}$  = 20.8 Hz,  ${}^{4}J_{F,H}$  = 5.9 Hz, 1 F, Ar-F).

The following compounds according to the invention are obtained analogously to Example 1 using the corresponding precursors:

#### Examples 2-126

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$$R^{1}$$
 $CF_{2}O$ 
 $L^{4}$ 
 $L^{1}$ 
 $R^{2}$ 
 $L^{3}$ 
 $L^{2}$ 

20

#### **Examples 127-252**

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$$R^1$$
  $CF_2CF_2$   $CF_2O$   $CF_$ 

#### **Examples 253-378**

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$$R^1$$
  $CH_2CH_2$   $CF_2O$   $CF_$ 

## Examples 379-504

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2}$$
 laa

	Exam	ples			R <sup>1</sup>	L <sup>1</sup>	$L^2$	$L^3$	L⁴	$R^2$
10	1.	127.	253.	379.	C <sub>3</sub> H <sub>7</sub>	F	F	Н	Н	F
	2.	128.	254.	380.	$C_3H_7$	F	Н	Н	Н	F
	3.	129.	255.	381.	$C_3H_7$	H	Н	Н	Н	F
	4.	130.	256.	382.	$C_2H_5$	Н	Н	Н	Н	F
15	<b>5</b> .	131.	<b>257</b> .	383.	$C_2H_5$	F	Н	Н	Н	F
	6.	132.	258.	384.	$C_2H_5$	F	F	Н	Н	F
	7.	133.	259.	385.	C₄H <sub>9</sub>	Н	Н	Н	Н	F
	8.	134.	260.	386.	C₄H <sub>9</sub>	F	Н	· H	Н	F
	9.	135.	261.	387.	C₄H <sub>9</sub>	F	F	Н	Н	F
20	10.	136.	262.	388.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	F
	11.	137.	263.	389.	$C_5H_{11}$	F	Н	Н	Н	F
	12.	138.	264.	390.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	F
	13.	139.	265.	391.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	F
25	14.	140.	266.	392.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	F
	<b>15</b> .	141.	267.	393.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	F
	16.	142.	268.	394.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	F
	17.	143.	269.	395.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	F
	18.	144.	270.	396.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	F
30	19.	145.	271.	397.	$C_2H_5$	Н	Н	Н	Н	CF <sub>3</sub>
	20.	146.	272.	398.	$C_2H_5$	F	Н	Н	Н	CF <sub>3</sub>
	21.	147.	273.	399.	$C_2H_5$	F	F	Н	Н	CF <sub>3</sub>
	22.	148.	274.	400.	$C_3H_7$	Н	Н	Н	Н	CF <sub>3</sub>
35	23.	149.	275.	401.	$C_3H_7$	F	Н	Н	Н	CF <sub>3</sub>
55	24.	150.	<b>276</b> .	402.	$C_3H_7$	F	F	Н	Н	CF <sub>3</sub>

Examp	les			R <sup>1</sup>	L <sup>1</sup>	L <sup>2</sup>	$L^3$	L <sup>4</sup>	$R^2$
25.	151.	277.	403.	C <sub>4</sub> H <sub>9</sub>	Н	Н	Н	Н	CF <sub>3</sub>
26.	152.	278.	404.	C₄H <sub>9</sub>	F	Н	Н	Н	CF <sub>3</sub>
27.	153.	279.	405.	C <sub>4</sub> H <sub>9</sub>	F	F	Н	Н	CF <sub>3</sub>
28.	154.	280.	406.	$C_5H_{11}$	Н	Н	Н	Н	CF <sub>3</sub>
29.	155.	281.	407.	$C_5H_{11}$	F	Н	Н	Н	CF <sub>3</sub>
30.	156.	282.	408.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	CF <sub>3</sub>
31.	157.	283.	409.	$C_6H_{13}$	Н	Н	Н	Н	CF <sub>3</sub>
32.	158.	284.	410.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	CF <sub>3</sub>
33.	159.	285.	411.	$C_6H_{13}$	F	F	Н	Н	CF <sub>3</sub>
34.	160.	286.	412.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	CF <sub>3</sub>
35.	161.	287.	413.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	CF <sub>3</sub>
36.	162.	288.	414.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	CF <sub>3</sub>
37.	163.	289.	415.	$C_2H_5$	Н	Н	Н	Н	OCF <sub>3</sub>
38.	164.	290.	416.	$C_2H_5$	F	Н	Н	Н	OCF <sub>3</sub>
39.	165.	291.	417.	$C_2H_5$	F	F	Н	Н	OCF <sub>3</sub>
<b>4</b> 0.	166.	292.	418.	C <sub>3</sub> H <sub>7</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
41.	167.	293.	419.	C <sub>3</sub> H <sub>7</sub>	F	Н	Н	Н	OCF <sub>3</sub>
42.	168.	294.	<b>420</b> .	$C_3H_7$	F	F	Н	Н	OCF <sub>3</sub>
43.	169.	295.	421.	C <sub>4</sub> H <sub>9</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
44.	170.	296.	<b>422</b> .	C₄H <sub>9</sub>	F	Н	Н	Н	OCF <sub>3</sub>
<b>45</b> .	171.	297.	<b>423</b> .	C₄H <sub>9</sub>	F	F	Н	Н	OCF <sub>3</sub>
46.	172.	298.	424.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
47.	173.	299.	<b>425</b> .	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	OCF <sub>3</sub>
48.	174.	300.	<b>426</b> .	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	OCF <sub>3</sub>
49.	175.	301.	427.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
50.	176.	302.	428.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	OCF <sub>3</sub>
51.	177.	303.	429.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	OCF <sub>3</sub>
52.	178.	304.	430.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
53.	179.	305.	431.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	OCF <sub>3</sub>
54.	180.	306.	432.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	OCF <sub>3</sub>
55.	181.	307.	433.	$C_2H_5$	Н	Н	H	Н	CN
56.	182.	308.	434.	$C_2H_5$	F	Н	Н	Н	CN

	Examp	oles			$R^1$	L <sup>1</sup>	L <sup>2</sup>	$L^3$	L <sup>4</sup>	$R^2$
	57.	183.	309.	435.	C₂H₅	F	F	Н	Н	CN
	58.	184.	310.	436.	C <sub>3</sub> H <sub>7</sub>	Н	Н	Н	Н	CN
_	59.	185.	311.	437.	$C_3H_7$	F	Н	Н	Н	CN
5	60.	186.	312.	438.	C <sub>3</sub> H <sub>7</sub>	F	F	Н	Н	CN
	61.	187.	313.	439.	C₄H <sub>9</sub>	Н	Н	Н	Н	CN
	62.	188.	314.	440.	C₄H <sub>9</sub>	F	Н	Н	Н	CN
	63.	189.	315.	441.	C₄H <sub>9</sub>	F	F	Н	Н	CN
10	64.	190.	316.	442.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	CN
	65.	191.	317.	443.	C <sub>5</sub> H <sub>11</sub>	F	Н	H	Н	CN .
	66.	192.	318.	444.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	CN
	<b>67</b> .	193.	319.	445.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	CN
4.5	68.	194.	320.	446.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	CN
15	69.	195.	321.	447.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	CN
	70.	196.	322.	448.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	CN
	71.	197.	323.	449.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	CN
	72.	198.	324.	<b>450</b> .	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	CN
20	73.	199.	325.	<b>451</b> .	$C_2H_5$	Н	Н	Н	Н	NCS
	74.	200.	326.	452.	$C_2H_5$	F	Н	·Η	Н	NCS
	<b>75</b> .	201.	327.	<b>453</b> .	$C_2H_5$	F	F	Н	Н	NCS
	76.	202.	328.	<b>454</b> .	$C_3H_7$	Н	Н	Н	Н	NCS
	<b>77</b> .	203.	329.	455.	$C_3H_7$	F	Н	Н	Н	NCS
25	78.	204.	330.	<b>456</b> .	$C_3H_7$	F	F	Н	Н	NCS
	79.	205.	331.	<b>457</b> .	C₄H <sub>9</sub>	Н	Н	Н	Н	NCS
	80.	206.	332.	<b>458</b> .	C <sub>4</sub> H <sub>9</sub>	F	Н	Н	Н	NCS
	81.	207.	333.	<b>459</b> .	C₄H <sub>9</sub>	F	F	Н	Н	NCS
30	82.	208.	334.	460.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	NCS
	83.	209.	335.	461.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	NCS
	84.	210.	336.	462.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	NCS
	<b>85</b> .	211.	337.	463.	$C_6H_{13}$	Н	Н	Н	Н	NCS
	86.	212.	338.	464.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	NCS
35	87.	213.	339.	465.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	NCS
	88.	214.	340.	466.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	NCS

	Exam	ples			R <sup>1</sup>	L <sup>1</sup>	L <sup>2</sup>	L <sup>3</sup>	L <sup>4</sup>	$R^2$
	89.	215.	341.	467.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	NCS
	90.	216.	342.	<b>468</b> .	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	NCS
5	91.	217.	343.	<b>469</b> .	C <sub>2</sub> H <sub>5</sub>	Н	Н	Н	Н	SF <sub>5</sub>
5	92.	218.	344.	<b>470</b> .	C <sub>2</sub> H <sub>5</sub>	F	Н	Н	Н	SF₅
	93.	219.	345.	471.	$C_2H_5$	F	F	Н	Н	SF <sub>5</sub>
	94.	220.	346.	472.	$C_3H_7$	Н	Н	Н	Н	SF <sub>5</sub>
	95.	221.	347.	<b>473</b> .	$C_3H_7$	F	Н	Н	Н	SF <sub>5</sub>
10	96.	222.	348.	<b>474</b> .	$C_3H_7$	F	F	Н	Н	SF <sub>5</sub>
	97.	223.	349.	<b>475</b> .	C₄H <sub>9</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	98.	224.	350.	<b>476</b> .	C₄H <sub>9</sub>	F	Н	Н	Н	SF <sub>5</sub>
	99.	225.	351.	<b>477</b> .	C₄H <sub>9</sub>	F	F	Н	Н	SF <sub>5</sub>
4.5	100.	226.	<b>352</b> .	478.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	SF <sub>5</sub>
15	101.	<b>227</b> .	<b>353</b> .	<b>479</b> .	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	SF <sub>5</sub>
	102.	228.	<b>354</b> .	480.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	SF <sub>5</sub>
	103.	229.	355.	481.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	104.	230.	<b>356</b> .	482.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	SF <sub>5</sub>
20	105.	231.	<b>357</b> .	483.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	SF <sub>5</sub>
	106.	232.	<b>358</b> .	484.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	107.	233.	359.	485.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	SF <sub>5</sub>
	108.	234.	360.	486.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	SF <sub>5</sub>
	109.	235.	361.	487.	C <sub>2</sub> H <sub>5</sub>	Н	Н	Н	Н	OC <sub>2</sub> H <sub>5</sub>
25	110.	236.	362.	488.	$C_2H_5$	F	Н	Н	Н	OC <sub>2</sub> H <sub>5</sub>
	111.	237.	363.	489.	$C_2H_5$	F	Н	F	Н	OC <sub>2</sub> H <sub>5</sub>
	112.	238.	364.	490.	$C_3H_7$	Н	Н	Н	Н	$OC_2H_5$
	113.	239.	365.	491.	$C_3H_7$	F	Н	Н	Н	OC <sub>2</sub> H <sub>5</sub>
30	114.	240.	366.	492.	$C_3H_7$	F	Н	F	Н	$OC_2H_5$
	115.	241.	367.	493.	C₄H <sub>9</sub>	Н	Н	Н	Н	$OC_2H_5$
	116.	242.	368.	494.	C₄H <sub>9</sub>	F	Н	Н	Н	$OC_2H_5$
	117.	243.	369.	<b>495</b> .	C₄H <sub>9</sub>	F	Н	F	Н	OC <sub>2</sub> H <sub>5</sub>
	118.	244.	370.	<b>496</b> .	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	OC <sub>2</sub> H <sub>5</sub>
35	119.	245.	371.	<b>497</b> .	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	OC <sub>2</sub> H <sub>5</sub>
	120.	246.	372.	498.	C <sub>5</sub> H <sub>11</sub>	F	Н	F	Н	OC <sub>2</sub> H <sub>5</sub>

Exam	ples	•		$R^1$	$L^1$	L²	$L^3$	L <sup>4</sup>	$R^2$
121.	247.	373.	499.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	OC₂H₅
122.	248.	374.	500.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	OC₂H₅
123.	249.	375.	501.	C <sub>6</sub> H <sub>13</sub>	F	Н	F	Н	$OC_2H_5$
124.	250.	376.	502.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	OC₂H₅
125.	251.	377.	503.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	OC₂H₅
126.	252.	378.	504.	C <sub>7</sub> H <sub>15</sub>	F	Н	F	Н	OC <sub>2</sub> H <sub>5</sub>

5

### Example 505

The compound of the following formula

15

$$C_3H_7$$
  $CF_2O$   $F$ 

20

2-(difluoro[3,4,5-trifluorophenyl]oxymethyl)-7-(4-n-propylcyclohexyl)spiro-[5.3]nonane (11)

is prepared as follows:

25

2-(difluoro[3,4,5-trifluorophenyl]oxymethyl)-7-(4-n-propylcyclohexyl)spiro-[5.3]nonane (11) is obtained from 7-(4-n-propylcyclohexyl)spiro[5.3]nonan-2-one (9) analogously to the synthesis described in Example 1.

$$C_3H_7$$
  $C_3H_7$   $O$ 

10 8.90 g (32.0 mmol) of the dithioacetal 10 are dissolved in 80 ml of dichloromethane, and 2.8 ml (32.0 mmol) of trifluoromethanesulfonic acid are added dropwise with ice/common salt cooling. After 5 minutes, the cooling is removed, and the batch is stirred at room temperature for 45 minutes. The batch is subsequently cooled to -70°C, a mixture of 7.1 ml 15 (51.0 mmol) of triethylamine and 7.10 g (48.0 mmol) of trifluorophenol in 80 ml of dichloromethane is added, and the batch is stirred at -70°C for 1 hour. 25.8 ml (0.160 mol) of triethylamine tris(hydrofluoride) are then added, and, after 5 minutes, 45.8 g (0.150 mol) of DBH, suspended in 60 ml of dichloromethane, are added in portions over the course of about 20 30 minutes. After 90 minutes, the batch is allowed to thaw and is hydrolysed using 1 M sodium hydroxide solution and aqueous hydrogen sulfite solution. The organic phase is separated off, washed with saturated sodium chloride solution and dried over sodium sulfate. The solvent is removed under reduced pressure, and the residue is filtered through silica 25 gel with n-heptane. The crude product is purified by bulb-tube distillation (boiling point: 158°C/0.1 mbar), giving the spiro compound 11.

$$\Delta \varepsilon = 7.4$$
 $\Delta n = 0.0641$ 

The following compounds according to the invention are obtained analogously to Example 505 using the corresponding precursors:

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## **Examples 506-630**

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2}$$
 Iba

#### 10 **Examples 631-756**

$$R^{1} \longrightarrow CF_{2}O \longrightarrow R^{2} \qquad Ibb$$

## **Examples 757-882**

20

25

35

$$R^1$$
  $CF_2CF_2$   $CF_2O$   $CF_$ 

## Examples 883-1008

$$R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow CF_{2}O \longrightarrow L^{3} \longrightarrow L^{2}$$
 Ibb

	Examp	les			R <sup>1</sup>	L <sup>1</sup>	L <sup>2</sup>	$L^3$	L <sup>4</sup>	$R^2$
	505.	631.	757.	883.	C <sub>3</sub> H <sub>7</sub>	F	F	Н	Н	F
	506.	632.	<b>758</b> .	884.	$C_3H_7$	F	Н	Н	Н	F
-	507.	633.	<b>759</b> .	885.	C <sub>3</sub> H <sub>7</sub>	Н	Н	Н	Н	F
5	508.	634.	760.	886.	$C_2H_5$	Н	Н	Н	Н	F
	509.	635.	761.	887.	C <sub>2</sub> H <sub>5</sub>	F	Н	Н	Н	F ·
	510.	636.	762.	888.	C <sub>2</sub> H <sub>5</sub>	F	F	Н	Н	F
	511.	637.	763.	889.	C₄H <sub>9</sub>	Н	Н	Н	Н	F
10	512.	638.	764.	890.	C₄H <sub>9</sub>	F	Н	Н	Н	F
	513.	639.	765.	891.	C <sub>4</sub> H <sub>9</sub>	F	F	Н	Н	F
	514.	640.	766.	892.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	F
	515.	641.	767.	893.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	F
4 ==	516.	642.	768.	894.	C₅H <sub>11</sub>	F	F	Н	Н	F
15	517.	643.	<b>76</b> 9.	895.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	F
	518.	644.	<b>770</b> .	896.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	F
	519.	645.	771.	897.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	F
	<b>520</b> .	646.	772.	898.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	F
20	521.	647.	773.	899.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	F
	<b>522</b> .	648.	774.	900.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	F
	<b>523</b> .	649.	775.	901.	$C_2H_5$	Н	Н	Н	Н	CF₃
	524.	650.	776.	902.	$C_2H_5$	F	Н	Н	Н	CF₃
	<b>525</b> .	651.	777.	903.	$C_2H_5$	F	F	Н	Н	CF <sub>3</sub>
25	526.	<b>652</b> .	778.	904.	$C_3H_7$	Н	Н	Н	Н	CF₃
	<b>527</b> .	653.	779.	905.	$C_3H_7$	F	Н	Н	Н	CF₃
	528.	<b>654</b> .	<b>780</b> .	906.	$C_3H_7$	F	F	Н	Н	CF₃
	529.	655.	781.	907.	C₄H <sub>9</sub>	Н	Н	Н	Н	CF₃
30	530.	656.	782.	908.	C <sub>4</sub> H <sub>9</sub>	F	Н	Н	Н	CF <sub>3</sub>
	531.	657.	783.	909.	C₄H <sub>9</sub>	F	F	Н	Н	CF <sub>3</sub>
	532.	<b>658</b> .	784.	910.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	CF <sub>3</sub>
	533.	659.	785.	911.	C <sub>5</sub> H <sub>11</sub> .	F	Н	Н	Н	CF <sub>3</sub>
	534.	660.	786.	912.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	CF <sub>3</sub>
35	535.	661.	787.	913.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	CF <sub>3</sub>
	536.	662.	788.	914.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	CF <sub>3</sub>

	Examp	oles			R <sup>1</sup>	L <sup>1</sup>	L <sup>2</sup>	$L^3$	L <sup>4</sup>	$R^2$
	537.	663.	789.	915.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	CF <sub>3</sub>
	538.	664.	790.	916.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	CF <sub>3</sub>
-	539.	665.	791.	917.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	CF <sub>3</sub>
5	540.	666.	<b>792</b> .	918.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	CF <sub>3</sub>
	541.	667.	793.	919.	$C_2H_5$	Н	Н	Н	Н	OCF <sub>3</sub>
	542.	668.	794.	920.	$C_2H_5$	F	Н	Н	Н	OCF <sub>3</sub>
	543.	669.	795.	921.	$C_2H_5$	F	F	Н	Н	OCF <sub>3</sub>
10	544.	670.	796.	922.	$C_3H_7$	Н	Н	Н	Н	OCF <sub>3</sub>
	<b>545</b> .	671.	797.	923.	$C_3H_7$	F	Н	Н	Н	OCF <sub>3</sub>
	546.	672.	798.	924.	$C_3H_7$	F	F	Н	Н	OCF <sub>3</sub>
	547.	673.	799.	925.	C <sub>4</sub> H <sub>9</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
	548.	674.	800.	926.	C₄H <sub>9</sub>	F	Н	Н	Н	OCF <sub>3</sub>
15	549.	675.	801.	927.	C₄H <sub>9</sub>	F	F	Н	Н	OCF <sub>3</sub>
	550.	676.	802.	928.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
	551.	677.	803.	929.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	OCF <sub>3</sub>
	552.	678.	804.	930.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	OCF <sub>3</sub>
20	553.	679.	805.	931.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
	554.	680.	806.	932.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	OCF₃
	555.	681.	807.	933.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	OCF <sub>3</sub>
	556.	682.	808.	934.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	OCF <sub>3</sub>
	557.	683.	809.	935.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	OCF <sub>3</sub>
25	558.	684.	810.	936.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	OCF <sub>3</sub>
	559.	685.	811.	937.	C₂H₅	Н	Н	Н	Н	CN
	560.	686.	812.	938.	$C_2H_5$	F	Н	Н	Н	CN
	561.	687.	813.	939.	C <sub>2</sub> H <sub>5</sub>	F	F	Н	Н	CN
30	562.	688.	814.	940.	$C_3H_7$	Н	Н	Н	Н	CN
	563.	689.	815.	941.	$C_3H_7$	F	Н	Н	Н	CN
	564.	690.	816.	942.	$C_3H_7$	F	F	Н	Н	CN
	565.	691.	817.	943.	C₄H <sub>9</sub>	Н	Н	Н	Н	CN
	566.	<b>692</b> .	818.	944.	C <sub>4</sub> H <sub>9</sub>	F	Н	Н	Н	CN
35	567.	693.	819.	945.	C <sub>4</sub> H <sub>9</sub>	F	F	Η .	Н	CN
	568.	694.	820.	946.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	H	CN

	Examp	oles			$R^1$	L <sup>1</sup>	$L^2$	$L^3$	L⁴	$R^2$
	569.	695.	821.	947.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	CN
	570.	696.	822.	948.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	CN
-	571.	697.	823.	949.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	CN
5	572.	698.	824.	950.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	CN
	573.	699.	825.	951.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	CN
	574.	700.	826.	952.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	CN
	575.	701.	827.	953.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	CN
10	576.	702.	828.	954.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	CN
	577.	703.	829.	955.	$C_2H_5$	Н	Н	Н	Н	NCS
	578.	704.	830.	956.	$C_2H_5$	F	Н	Н	Н	NCS
	579.	705.	831.	957.	$C_2H_5$	F	F	Н	Н	NCS
	580.	706.	832.	958.	$C_3H_7$	Н	Н	Н	Н	NCS
15	581.	707.	833.	959.	$C_3H_7$	F	Н	Н	Н	NCS
	582.	708.	834.	960.	$C_3H_7$	F	F	Н	Н	NCS
	583.	709.	835.	961.	C₄H <sub>9</sub>	Н	Н	Н	Н	NCS
	584.	710.	836.	962.	C₄H <sub>9</sub>	F	Н	Н	Н	NCS
20	585.	711.	837.	963.	C₄H <sub>9</sub>	F	F	Н	Н	NCS
	586.	712.	838.	964.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	NCS
	587.	713.	839.	965.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	NCS
	588.	714.	840.	966.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	NCS
	589.	715.	841.	967.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	NCS
25	590.	716.	842.	968.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	NCS
	591.	717.	843.	969.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	NCS
	592.	718.	844.	970.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	NCS
	593.	719.	845.	971.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	NCS
30	594.	<b>720</b> .	846.	972.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	NCS
	595.	721.	847.	973.	$C_2H_5$	Н	Н	Н	Н	SF <sub>5</sub>
	596.	<b>722</b> .	848.	974.	$C_2H_5$	F	Н	Н	Н	SF <sub>5</sub>
	597.	<b>723</b> .	849.	975.	C <sub>2</sub> H <sub>5</sub>	F	F	Н	Н	SF <sub>5</sub>
	598.	724.	<b>850</b> .	976.	$C_3H_7$	Н	Н	Н	Н	SF <sub>5</sub>
35	599.	725.	851.	977.	C <sub>3</sub> H <sub>7</sub>	F	Н	Н	Н	SF <sub>5</sub>
	600.	726.	<b>852</b> .	978.	C <sub>3</sub> H <sub>7</sub>	F	F	Н	Н	SF <sub>5</sub>

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	Exam	ples			R <sup>1</sup>	L <sup>1</sup>	L <sup>2</sup>	$L^3$	L <sup>4</sup>	$R^2$
	601.	727.	853.	979.	C <sub>4</sub> H <sub>9</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	602.	728.	854.	980.	$C_4H_9$	F	Н	Н	Н	SF <sub>5</sub>
5	603.	729.	855.	981.	C <sub>4</sub> H <sub>9</sub>	F	F	Н	Н	SF <sub>5</sub>
5	604.	730.	856.	982.	C₅H <sub>11</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	605.	731.	857.	983.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	SF <sub>5</sub>
	606.	732.	858.	984.	C <sub>5</sub> H <sub>11</sub>	F	F	Н	Н	SF₅
	607.	733.	859.	985.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	SF <sub>5</sub>
10	608.	734.	860.	986.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	SF <sub>5</sub>
	609.	735.	861.	987.	C <sub>6</sub> H <sub>13</sub>	F	F	Н	Н	SF <sub>5</sub>
	610.	736.	862.	988.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	SF <sub>5</sub>
	611.	737.	863.	989.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	SF <sub>5</sub>
45	612.	738.	864.	990.	C <sub>7</sub> H <sub>15</sub>	F	F	Н	Н	SF <sub>5</sub>
15	613.	739.	865.	991.	$C_2H_5$	Н	Н	Н	Н	$OC_2H_5$
	614.	740.	866.	992.	$C_2H_5$	F	Н	Н	Н	$OC_2H_5$
	615.	741.	867.	993.	$C_2H_5$	F	Н	F	Н	$OC_2H_5$
	616.	742.	868.	994.	$C_3H_7$	Н	Н	Н	Н	$OC_2H_5$
20	617.	743.	869.	995.	$C_3H_7$	F	Н	Н	Н	$OC_2H_5$
	618.	744.	870.	996.	$C_3H_7$	F	Н	F	Н	$OC_2H_5$
	619.	745.	871.	997.	C <sub>4</sub> H <sub>9</sub>	Н	Н	Н	Н	$OC_2H_5$
	620.	746.	872.	998.	C <sub>4</sub> H <sub>9</sub>	F	Н	Н	Н	$OC_2H_5$
	621.	747.	873.	999.	C <sub>4</sub> H <sub>9</sub>	F	Н	F	Н	$OC_2H_5$
25	622.	748.	874.	1000.	C <sub>5</sub> H <sub>11</sub>	Н	Н	Н	Н	$OC_2H_5$
	623.	749.	875.	1001.	C <sub>5</sub> H <sub>11</sub>	F	Н	Н	Н	$OC_2H_5$
	624.	<b>750</b> .	876.	1002.	<sup>-</sup> C <sub>5</sub> H <sub>11</sub>	F	Н	F	Н	$OC_2H_5$
	625.	751.	877.	1003.	C <sub>6</sub> H <sub>13</sub>	Н	Н	Н	Н	$OC_2H_5$
30	626.	<b>752</b> .	878.	1004.	C <sub>6</sub> H <sub>13</sub>	F	Н	Н	Н	$OC_2H_5$
	627.	753.	879.	1005.	C <sub>6</sub> H <sub>13</sub>	F	Н	F	Н	$OC_2H_5$
	628.	754.	880.	1006.	C <sub>7</sub> H <sub>15</sub>	Н	Н	Н	Н	$OC_2H_5$
	629.	755.	881.	1007.	C <sub>7</sub> H <sub>15</sub>	F	Н	Н	Н	$OC_2H_5$
	630.	756.	882.	1008.	C <sub>7</sub> H <sub>15</sub>	F	Н	F	Н	$OC_2H_5$
35										

9.90%

10.00%

## Example 1009

	A liquid-crystal mixture compris	sing
	BCH-3F.F	10.80%
5	BCH-5F.F	9.00%
	ECCP-3OCF <sub>3</sub>	4.50%
	ECCP-5OCF <sub>3</sub>	4.50%
	CBC-33F	1.80%
	CBC-53F	1.80%
10	CBC-55F	1.80%
	PCH-5F	9.00%
	PCH-6F	7.20%
	PCH-7F	5.40%
15	CCP-2OCF <sub>3</sub>	7.20%
	CCP-3OCF <sub>3</sub>	10.80%
	CCP-4OCF <sub>3</sub>	6.30%

# 20 has the following properties:

CCP-5OCF<sub>3</sub>

Clearing point: +86.0°C

Compound of Example 1

Δε: +5.6

Δn: +0.0924

# 25 <u>Example 1010</u>

## A liquid-crystal mixture comprising

30	CCH-3O1	11.23%
	CCH-3CF₃	6.42%
	CCH-5O1	8.82%
	CCP-2F.F.F	8.02%
	CCP-3F.F.F	10.42%
35	CCP-5F.F.F	4.01%
	CCPC-33	2.41%
	CCZU-2-F	4.01%
	CCZU-3-F	13.62%

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	CCZU-5-F	4.01%
	CH-33	2.41%
	CH-35	2.41%
	CH-43	2.41%
5	Compound of Example 1	19.80%

has the following properties:

Clearing point:

+72.0°C

Δn:

+0.0605

10

## Example 1011

A liquid-crystal mixture comprising

	•	•
15	BCH-3F.F	10.76%
	BCH-5F.F	8.98%
	ECCP-30CF <sub>3</sub>	4.49%
	ECCP-50CF <sub>3</sub>	4.49%
	CBC-33F	1.80%
20	CBC-53F	1.80%
	CBC-55F	1.80%
	PCH-6F	7.18%
	PCH-7F	5.39%
	CCP-20CF <sub>3</sub>	7.18%
25	CCP-30CF <sub>3</sub>	10.76%
	CCP-40CF <sub>3</sub>	6.28%
	CCP-50CF <sub>3</sub>	9.87%
	PCH-5F	8.98%
	Compound of Example 505	10.24%

30

has the following properties:

Clearing point:

+73.2°C

Δε:

+5.3

Δn:

+0.0885